

Achieving High Dopant Concentrations in Si: First Principles Simulations

*S.A. Centoni, B. Sadigh, M.J. Caturla, G.H. Gilmer,
T. Díaz de la Rubia*

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Achieving High Dopant Concentrations in Si: First Principles Simulations.

Scott A. Centoni, Babak Sadigh, Maria-Jose Caturla,
George H. Gilmer and Tomas Diaz de la Rubia

Lawrence Livermore National Laboratory, Livermore, CA 94550

ABSTRACT

In this paper we discuss methods to obtain high dopant concentrations during processing of Si devices. The possibility of increasing the solubility of B in Si by misfit stress is investigated. The enthalpy of B atoms is calculated, with and without stress, using density functional theory. A second approach, the trapping of excess dopant atoms during deposition of Si, is also considered. For this purpose, the enthalpies of several dopant species in sites near the surface are calculated.

1 INTRODUCTION

The design of efficient and compact Si devices can be facilitated by device processing simulations, provided the models are based on accurate kinetics to describe fabrication, including the diffusion and interactions of dopants and point defects [1]. In recent years the models of Si processing have improved significantly, due in part to data generated by quantum mechanics calculations based on density functional theory (DFT).

DFT calculations can also suggest new techniques for fabricating devices. The trend in integrated circuit fabrication is to pack the chips with higher densities of components, requiring high doping densities to provide sufficient current flow. We present DFT calculations of stress and its influence on equilibrium dopant concentrations that predict extremely large enhancements with biaxial stress from film/substrate misfit on the order of 1% [2]. Higher equilibrium solubility reduces the fraction of implanted dopant atoms that are in clusters and precipitates, and hence electrically inactive.

Another technique for doping at high concentrations is to deposit Si together with the dopant by chemical vapor deposition (CVD), or by co-deposition during molecular beam epitaxy (MBE) of silicon. In this way, the dopant is inserted without the need for energetic collisions with the Si crystal lattice. Therefore very little diffusion of dopant atoms or defects occurs, reducing the opportunity to form clusters and precipitates. The incorporation of impurities during deposition is strongly enhanced by surface segregation, and for this reason we will examine the energies of several dopant atoms in the vicinity of the surface.

2 STRESS AND B SOLUBILITY

During the past two decades much attention has been directed towards the study of the electronic properties of strained Si, as it has become possible to grow epitaxial interfaces between lattice mismatched materials; e.g. Si/Si_{1-x}Ge_x heterostructures [3]. The Si-B binary phase diagram indicates that for temperatures lower than 1200°C, the solid solubility of B in Si is smaller than 1 atomic percent [4]. Beyond this concentration, the excess B atoms form precipitates of the so-called SiB₃ phase. This phase has a complicated structure based on distorted boron-rich icosahedral clusters [4]. Assuming that the B concentration is dilute, the phase boundary between the bulk Si and SiB₃ phases is expressed as

$$[B]_{\max} = A \exp\{-(\Delta E_B - \mu_B - E_F)/kT\},$$

where $\mu_B = [E(B_3Si) - E(Si)]/3$, and $[B]_{\max}$ is the maximum soluble B concentration in Si, E_B is the energy of an isolated negatively charged B impurity, $E(B_3Si)$ and $E(Si)$ are the total energies per atom of the B₃Si and pure Si phases respectively, and A is a temperature independent prefactor which includes the vibrational entropy. The explicit appearance of the Fermi level E_F is due to the charge of the B

impurity. At finite temperatures, however, E_F depends on the dopant concentration, and we can derive the expression

$$[B]_{\max} = \sqrt{A n_i(T)} \exp\{-(\Delta E_B - \mu_B - E_{\text{mid}})/2kT\}$$

where n_i is the intrinsic carrier concentration and E_{mid} is the level at midgap [2].

We calculate the terms in the exponential in the above equation from first principles using the VASP plane-wave pseudopotential code [5] with Vanderbilt's ultrasoft pseudopotentials [6], supplied by G. Kresse and J. Hafner [7]. To calculate ΔE_B , we use a 128 atom supercell. The experimental ESL of B over the range 900° to 1325°C, exhibits Arrhenius behavior, i.e. $[B] \propto \exp(-E/kT)$, where $E = 0.73 \pm 0.04$ eV [8]. We can thus neglect the variation with strain of A and the chemical potential μ_B , in expression for $[B]_{\max}$ above.

Figure 1a depicts the change in ΔE_B and E_{mid} with bi-axial strain. It is shown that both these quantities depend linearly upon strain in such a way as to raise the B solubility for $\epsilon < 0$. But the change in E_{mid} with strain is an order of magnitude larger than the change in ΔE_B . Hence the strain dependence of the solubility of B in Si is determined to a large extent by the explicit response of the Si band structure to shear stress.

Figure 1 shows both GW and LDA results for the strain dependence of E_g and E_{mid} , from which we can conclude that LDA is very accurate for the strain dependence of the band structure of Si, in spite of its failure to correctly predict the Si band gap at equilibrium.

The intrinsic carrier concentration n_i in Si can be written as $n_i(T, \epsilon) = \rho(T, \epsilon) \exp(E_g/2kT)$, where $\rho(T, \epsilon)$ is a well-known function of the electronic density-of-states of Si, near the top of the valence band and the bottom of the conduction band.

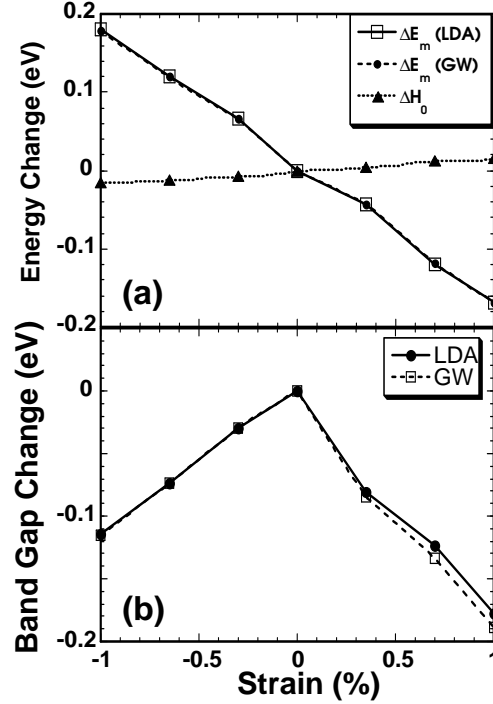


Figure 1. (a) shows the strain dependence of E_{mid} as well as ΔE_B . (b) shows the strain dependence of the band gap. All energies are relative to the cubic phase.

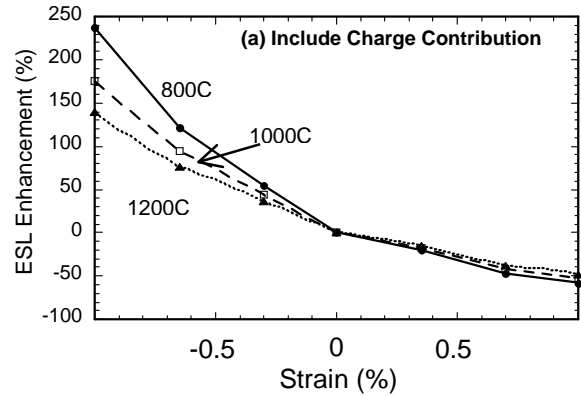


Figure 2. The enhancement of the solubility of boron as a function of strain at three temperatures.

From the above equation for $[B]_{\max}$ we can now calculate the strain dependence of the B solubility in Si (see Fig. 2a). We find that compressive bi-axial strain enhances the ESL of B dramatically. A 1% reduction in a_{parallel} can raise $[B]_{\max}$ by more than 150% at 1000°C. This is a remarkable result. Calculations were performed omitting the dependence of the Fermi level on the strain, and these showed a mere 15% increase in the

ESL at 1000°C, with 1% bi-axial compression. The opposite effect is expected for positively charged dopants such as As, where tensile strain would be expected to increase solubility.

3 SEGREGATION OF DOPANTS

Though the solubility limit of carbon in Si is only about $3 \times 10^{17} \text{ cm}^{-3}$ [9], films have been grown using MBE having concentrations as high as 10^{22} cm^{-3} , or 20% [10]. Tersoff used an empirical potential to examine a possible explanation for this based upon an increased solid solubility near the surface, which is frozen in as the film grows [11]. He predicted an equilibrium concentration limit near the surface of around $3 \times 10^{21} \text{ cm}^{-3}$, close to the MBE value above.

Crystal growth is inherently a non-equilibrium process, and trapping of a species at concentrations far above its maximum equilibrium value is always possible. The amount trapped will depend on the rate of crystal growth compared to the rate at which the impurity can diffuse away from the moving crystal surface. During MBE growth of Si with the co-deposition of dopant atoms, diffusion away from the surface is difficult or nearly impossible, since the evaporation rate for most dopants is small. Either they accumulate on the surface, or they are trapped in the growing crystal.

A high concentration of dopant present at the surface, increases the probability for dopant incorporation at advancing step edges. The energies of dopant atoms in sites near the surface can play an important role in trapping. Relatively low energies in these sites permit the large surface accumulation of dopant atoms to become incorporated at high concentrations in this region. Then, as the crystal grows, and the potential energies of the dopant atoms increase, their ability to hop to lower energy sites closer to the surface is impeded by the presence of several crystalline layers. Dopants with the lowest energies in these sites are expected to exhibit the highest supersaturations in the crystal.

We have calculated the energies of atoms at the surface sites by similar methods to those described above. A $4 \times 4 \times 7$ slab of silicon was

modeled, using periodic boundary conditions in the lateral directions (see Fig. 3).

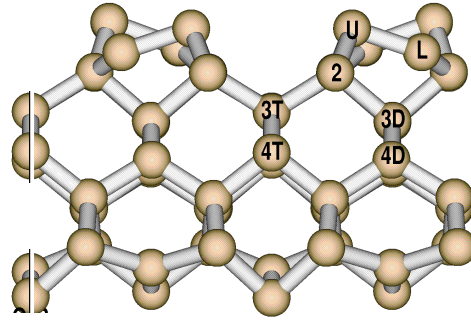


Figure 3. Atomic sites near the surface of a Si crystal. U and L are the upper and lower atoms of the tilted surface dimer, 2 indicates atoms in the second layer, 3T and 4T the third and fourth layer sites below the trench, and 3D and 4D are the sites below the dimer.

Energies obtained for dopant atoms in sites near the surface are shown in Fig. 4. The symbols indicate the sites marked in Fig. 3. We will discuss the differences in the behavior of the different dopant atoms in a forthcoming publication, together with comparisons with MBE data on trapping in excess of equilibrium solubilities. But the tendency to segregate at near-surface sites is common to all four dopants. It may be significant that the highest concentration relative to bulk Si solubility is found for MBE growth of C co-deposited with Si, since C has low energy surface sites, as seen in Fig. 4.

4 CONCLUSIONS

We have investigated two techniques to increase dopant concentrations in Si. The first involves ion-implanting B atoms into a strained layer of Si, grown epitaxially on the (001) surface of a slightly smaller pseudomorphic compound, such as ZnS. We attribute this effect largely to the charge of the B impurity in Si.

The second approach is to co-deposit silicon with the dopant atoms, using CVD or MBE methods. Dopant atoms may be trapped in the growing crystal at concentrations up to five orders of magnitude greater than their equilibrium solubility. We examined segregation of the dopant at sites near the surface of the crystal, and found some sites near

the surface where the concentration of the impurity would be enhanced by several orders of magnitude. Tersoff's results showing that there is a tendency for dopants to segregate in this region is qualitatively correct, although the various dopant species have very different behavior [11]. Strong segregation implies that a large dopant concentration is in the region being encompassed by the growing crystal, therefore likely to be trapped.

Acknowledgments

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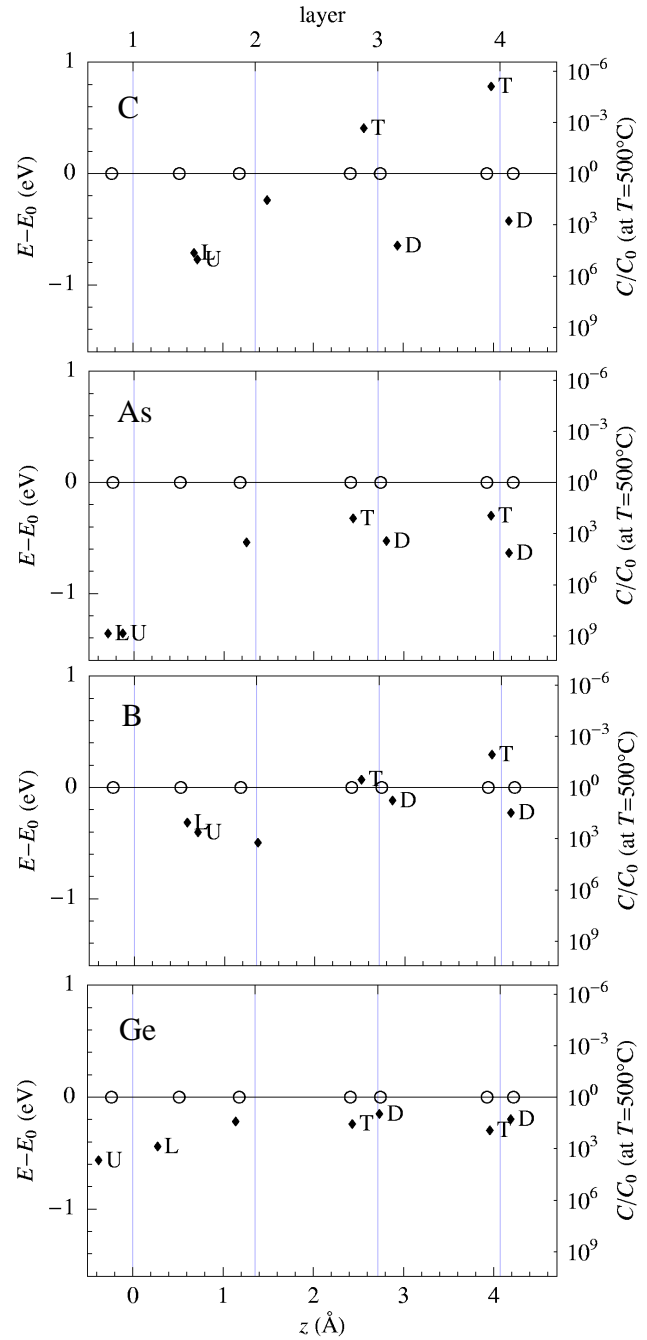


Figure 4. Energies of substitutional dopant atoms in sites near the surface, relative to their energies in the bulk Si. See Fig. 3 for identification of the sites corresponding to the symbols.